(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 694 631 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
28.10.1998 Bulletin 1998/44

(51) Int Cl.[6]: **C23C 18/31**, B29B 15/14

(21) Application number: **95111657.3**

(22) Date of filing: **25.07.1995**

(54) A surface-treated metal wire for use in the manufacture of elastomeric reinforced articles and a process for its manufacture

Oberflächenbehandelter Metalldraht zur Herstellung von verstärkten, elastomeren Gegenständen und Verfahren zu seiner Herstellung

Fil métallique traité en surface utilisé pour la fabrication d'articles renforcés en matière élastomère et son procédé de fabrication

(84) Designated Contracting States:
AT BE DE ES FR GB LU NL PT SE
Designated Extension States:
SI

(30) Priority: **28.07.1994 IT MI941627**

(43) Date of publication of application:
31.01.1996 Bulletin 1996/05

(73) Proprietor: **PIRELLI COORDINAMENTO PNEUMATICI S.p.A.**
20126 Milano (IT)

(72) Inventors:
- **Cavallotti, Pietro**
  I-20131 Milan (IT)
- **Pavan, Federico**
  I-50136 Firenze (IT)

(74) Representative: **Giannesi, Pier Giovanni et al**
Pirelli S.p.A.
Direzione Proprietà Industriale
Viale Sarca, 222
20126 Milano (IT)

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- **PATENT ABSTRACTS OF JAPAN vol. 9 no. 180 (C-293) ,25 July 1985 & JP-A-60 050175 (NIPPON PAINT K. K.) 19 March 1985,**

EP 0 694 631 B1

Description

The invention relates to a surface-treated metal wire for use in the realization of reinforcement structures for products made in elastomer material, of the type comprising a steel core provided with a metal alloy surface cladding.

The invention also relates to a process for realizing the surface-clad metal wire, as well as a reinforcement structure obtained with cords realized with the metal wire and a tyre or other product made in elastomer material incorporating the reinforcement structure.

In particular, the metal wire of the invention is destined to be subjected to usual stranding operations to obtain the cords to be used in making reinforcement structures for tyres and the like.

It is well known that tyres for vehicle wheels, as well as other manufactured products in elastomer material, usually incorporate reinforcement structures made from cords, each composed of a plurality of metal wires specially interconnected by means of usual stranding and twisting operations.

Normally the metal wires have a steel core on which a metal alloy cladding is deposited, said alloy having the double function of protecting the wire from corrosion and of guaranteeing a good adhesion of the elastomer on the metal reinforcement structure.

Commonly the alloy used for cladding the wires is brass; more precisely, a copper/zinc alloy containing about 70% copper and 30% zinc.

In prior art alloys of this kind, numerous attempts to obviate the typical drawbacks inherent in their use have been made: such alloys are in fact notorious for the fact that on ageing their adhesion to the elastomer deteriorates due to a process of diffusion of the copper ions into the elastomer, which process also alters the mechanical characteristics of the elastomer.

For instance, Japanese publication JP 01-031,837 teaches cladding a steel wire with a non-ferrous metal, such as Cu, Zn, Mn, Sn or alloys thereof, with a layer of cobalt deposited on the alloys: adhesion is therefore achieved between the cobalt layer and the suitably-processed elastomer mix, which latter is obtained through addition of cobalt salts or other suitable adhesion-enhancers.

US 4,677,033 discloses a steel-core metal wire clad with a ternary alloy composed of copper, zinc and manganese, the manganese being concentrated to a level of between 0.01% and 5% on the periphery of the cladding.

US 4,704,337 teaches the application of a usual brass cladding on the metal core of the wire, on which cladding an external layer of a very hard material is deposited, chosen from a group comprising Fe, Mn, Cr, Mo, V, Ti, Zr, Ta, Hf and W.

The following alloys are also known from the prior art: zinc/cobalt and/or zinc/nickel, in single or double layers.

The present invention discloses that by realizing a cladding by means of a binary alloy of zinc/manganese, with manganese levels chosen from a range comprised between 5% and 80%, it is possible to obtain an exceptionally good protection of the steel core from corrosion, without even minimally penalizing (with respect to usual brass alloys) the adhesion quality thereof with the elastomer mix, and what is more obtaining a surprisingly good drawability of the surface-treated wires.

In particular, the invention relates to a surface-treated metal wire for realizing reinforcement structures in elastomer material products, characterised in that the surface cladding is constituted by a zinc/manganese alloy, with a manganese content comprised between 5% amd 80%.

In a preferred embodiment the manganese content is comprised between 30% and 70%.

More in detail, the surface cladding layer is formed by electrodeposition on the surface of the steel core, and exhibits after drawing a thickness comprised between 0.1 and 0.35 microns, the total diameter of the wire being comprised between 0.15 and 0.35 mm.

In the present invention, in a first embodiment the metal wire is made by a process characterised in that it comprises at least one immersion phase of the steel core in an electrolytic bath containing zinc sulphate and manganese sulphate, to cause deposition of the cladding layer, which layer is composed therefore of a zinc/manganese alloy with manganese content comprised between 5% and 80%.

More in detail, the electrolytic bath is constituted by a water solution containing:

- zinc sulphate heptahydrate at between 10 and 90 gr/litre;
- manganese sulphate monohydrate at between 20 and 100 gr/litre;
- sodium citrate at between 115 and 230 gr/litre.

The electrolytic bath is advantageously maintained at a temperature comprised between 20 degrees and 60 degrees celsius, with a pH value of between 4 and 6.

A cathodic current density of between 5 and 40 A/dmq is applied to the electrolytic bath.

Alternatively, according to a further embodiment of the invention, the layers of zinc and manganese are deposited separately on the wire, and are heat diffused to constitute the alloy cladding.

A first further process embodiment comprises the phases of:

- immersion of the steel core in at least a first electrolytic bath containing manganese sulphate, to cause electrodeposition of manganese on the external surface of the core;
- immersion of the steel core in a second electrolytic bath containing zinc sulphate, to cause deposition of zinc on the external surface of the core;

- heat diffusion of the zinc and manganese to form the layer of zinc/manganese alloy.

More specifically, the first electrolytic bath comprises a water solution containing:

- manganese sulphate monohydrate at a level comprised between 80 and 120 gr/litre;
- ammonium sulphate comprised between 60 and 90 gr/litre; and
- ammonium thiocyanate comprised between 40 and 80 gr/litre.

The first electrolytic bath is maintained at a temperature chosen from a range of between 20 degrees celsius and 40 degrees, with pH values comprised between 4.5 and 5.5, preferably 5.

Cathodic current density comprised between 15 and 25 A/dmq is applied to the first electrolytic bath.

A second electrolytic bath contains:

- zinc sulphate heptahydrate at between 300 and 450 gr/litre;
- sodium sulphate at between 50 and 70 gr/litre.

The second bath is maintained at a temperature of between 20 and 30 degrees celsius, with pH value comprised between 2 and 4.

Cathodic current density in the second electrolytic bath is applied at between 20 and 40 A/dmq.

Advantageously the heat diffusion phase is effected through heating by Joule effect of the metal wire.

In a second process embodiment, the compositions of the first and the second electrolytic bath are inverted.

Further characteristics and advantages of the present invention will better emerge from the detailed description that follows, of some preferred embodiments of the surface-treated metal wire for realizing reinforcement structures for elastomer products, and of the process for obtaining the surface cladding, illustrated in the form of a non-limiting example in the accompanying drawings, in which:

Figure 1 is a graph which, with reference to a metal wire according to the invention, illustrates rust formation times on the y-ordinates according to the precentage of manganese in the zinc/manganese alloy deposited on the steel core;

Figure 2 is a table of comparisons with reference to rust-resistance in saline displayed by samples of the metal wire of the invention, in relation to that of other metal wire samples made according to various prior art processes;

Figure 3 is a graph expressing the drawability of the metal wire of the invention, expressed on the ordinates as a quantity of exfoliated cladding in relation to the precentage of manganese in the zinc/manganese alloy deposited on the steel core;

Figure 4 is a table of comparisons with reference to rubber-metal adhesion durability obtained by the process of the present invention, with respect to prior art cladding processes.

The metal wire of the invention exhibits a steel core provided with a metal alloy surface cladding, which has the double aim of protecting the core from corrosion and of guaranteeing good adhesion of the wire to the elastomer which it will be incorporated in.

Further, the surface cladding must endow the metal wire with good drawability, to ease the drawing operations which will be carried out on the wire after deposition of the surface cladding.

In the present invention the surface cladding is constituted by a zinc/manganese alloy, in which the manganese level is chosen from a range of between 5% and 80%, and the cladding is obtained by electrodeposition on the external surface of the steel core.

For this reason, in a first embodiment of the process of the invention, after a pickling phase in sulphuric acid or the like, the steel core, fed continuously from a reel, is introduced into an electrolytic bath containing zinc sulphate and manganese sulphate, to cause deposition of the zinc/manganese alloy on the core.

More in detail, the electrolytic bath is constituted by a water solution containing:

- zinc sulphate heptahydrate at a level comprised between 10 and 90 gr/litre;
- manganese sulphate monohydrate at a level comprised between 20 and 100 gr/litre, preferably at 30 gr/litre; and
- sodium cytrate at a level comprised between 115 and 230 gr/litre.

The temperature of the bath is preferably maintained constant within a field of between 20 and 60 degrees celsius.

The pH of the bath is maintained at between 4 and 6.

For the electrodeposition, stainless steel or zinc anodes can be used, and the cathodic current density in the bath is preferably comprised between 5 and 40 A/dmq.

It should be noted that the above-mentioned temperatures, pH values and anodic current density have been chosen in accordance with the percentage of manganese desired in the electrodeposited alloy.

The percentage level of manganese in the alloy tends to increase proportionally with the increase in the pH value, and the density of anodic current, and to diminish proportionally with the increase in the electrolytic bath temperature.

The feed velocity of the steel core from the reel and

thus the time it spends in the bath are regulated depending on the desired final thickness of the resulting cladding on the core.

In a preferred embodiment the final cladding thickness will be comprised between 1.5 and 4 microns, as the diameter of the steel core subjected to electrodeposition is comprised between 0.85 and 2mm.

When it leaves the electrolytic bath, the clad wire can be subjected to a further pickling phase or a phosphating bath, then to be rewound on a reel or directly subjected to one or more drawing operations, which bring the final diameter of the wire to a value comprised between 0.15 and 0.35 mm.

Alternatively to the above description, the formation of the surface coating on the steel core can be made by immersion thereof successively in a first and a second electrolytic bath by means of which first zinc and then manganese are deposited such that after a following heat diffusion phase by means of Joule effect the zinc/manganese alloy is created.

More in detail, the first electrolytic bath preferably comprises:

- manganese sulphate monohydrate in a quantity comprised between 80 and 120 gr/litre, preferably 100 gr/litre;
- ammonium sulphate in a quantity comprised between 60 and 90 gr/litre, preferably 75 gr/litre; and
- ammonium thiocyanate, in a quantity comprised between 40 and 80 gr/litre, preferably 60 gr/litre.

The first bath is maintained at a temperature of between 20 and 40 degrees celsius, preferably at 25 degrees, and has a pH of between 4.5 and 5.5, preferably 5.

For manganese electrodeposition, the anodes used are preferably graphite/manganese at a ratio of 8:1, while the cathodic current density is comprised between 15 and 25 A/dmq, preferably 20 A/dmq.

The second electrolytic bath is preferably constituted by a water solution containing:

- zinc sulphate heptahydrate at between 300 and 450 gr/litre, preferably 370 gr/litre;
- sodium sulphate at between 50 and 70 gr/litre, preferably 60 gr/litre.

The second bath is maintained at a temperature of between 20 and 30 degrees celsius, preferably at 25 degrees, with pH value comprised between 2 and 4, preferably 3.

For electrodeposition the anodes used are preferably zinc, and the cathodic current density applied is comprised between 20 and 40 A/dmq, preferably 30 A/dmq.

In a further embodiment, the order of the above first and the second baths is inverted, such that the zinc is electrodeposited before the manganese.

After electrodiffusion a pickling phase can be proceeded to, by means of a phosphating bath, and the resulting wire can be rewound on wheels or directly subjected to successive phases of drawing to bring it down to a desired diameter.

The advancement velocity of the wire from the reel and the length of time the steel core remains in the first and second electrolytic baths will be regulated such as to give the desired final thickness to the deposited cladding, as well as to obtain the desired percentage of manganese in the zinc/manganese alloy constituting the cladding.

It has been found that the zinc/manganese alloy surface cladding according to the present invention endows the treated wire with exceptional rust-resistant qualities, which tend to increase as the percentage of manganese in the alloy grows, as shown in the graph of figure 1.

More precisely, the graph of figure 1 shows, on the y-ordinates, the rust-formation times in minutes, with respect to the precentage of manganese in the zinc/manganese coating layer.

The graph relates to a test carried out by immersing test samples clad with a Zn/Mn alloy of 3 microns thickness in a water solution of NaCl at 5%.

It is easy to see how rust resistance qualities vary from a minimum of about 250 minutes, in a sample where Manganese was totally absent, up to a maximum of about 20,000 minutes, where the percentage of manganese was about 80%.

For the purposes of comparison, the table of figure 2 shows the minutes of rust resistance of the zinc/manganese clad samples where manganese percentages were at 5%, 30% and 80%, as well as the rust-resistance of corresponding samples clad in brass, Zn, Zn/Co, NiCo/ZnCo in a double layer.

Test conditions were the same as those described in reference to the graph of figure 1.

It can clearly be seen that with a manganese percentage of only 5% the resistance to rust is already more than 10 times the resistence of a normal brass cladding.

With manganese at 30% resistance to rust grows to over twice as much as that in the zinc/cobalt alloys, and is also decidedly superior to that of the NiZn/ZnCo double-layer claddings.

The wire treated according to the present invention further exhibits surprisingly good drawability properties, which was unexpected by the specialist as manganese is a notoriously hard substance and would lead to suppose the opposite.

However, notwithstanding the presuppositions, it was found that with the zinc/manganese cladding, especially if the manganese content is comprised between 30% and 70%, excellent drawability was possible with minimum exfoliation consequences when the wire was passed through the drawplate.

The graph of figure 3 expresses the drawability of the wire of the present invention in terms of quantity of exfoliated cladding, expressed in gr/mq on the ordi-

nates, in accordance with the percentage of manganese in the Zn/Mn alloy, expressed on the x-coordinate.

Also worthy of not is the fact that the present invention exhibits excellent adhesion characteristics to the elastomer material, which, as mentioned above, is fundamental to the mechanical resistance and durability of the tyres for vehicle wheels to which the invention will be applied in the form of a reinforcement structure made of webbing composed of stinging of the metal wire of the invention.

Figure 4, in fact, shows the durability of the adhesion of the invention to the elastomer, deriving from various tests made on rubber specimens containing adhesion enhancers based on cobalt, and vulcanized for thirty minutes at 151 degrees celsius; the specimens being tested with coatings of brass (70% copper, 30% zinc), zinc, zinc/manganese (manganese content varied between 5% and 80%), and with manganese alone.

The table clearly demonstrates how the zinc/manganese alloy results in no substantial qualitative decay in the rubber-metal adhesion in relation to the brass cladding.

The zinc/manganese alloy offers however the advantage of not bringing about qualitative decay in the rubber-metal adhesion over a considerable period of time, which is certainly not a characteristic of brass claddings, where the processes of dezincification and copper ion migration into the elastomer mix cause considerable decay.

It is strongly felt that the qualitative characteristics of the rubber-metal bond will be improved even more when further extensive testing leads to a refinement of the elastomer mix, especially with regard to better special adhesion enhancers and optimization of other factors such as, for example, the concentration of sulphur.

It is also felt that the drawability characteristics of the metal wire can be improved, with the application of special lubricants and/or suitable materials in the drawplates.

Particular attention is drawn to the fact that the present invention, thanks to the total absence of nickel in the process, obviates all problems of a sanitary nature which are normally connected with that metal in cladding processes involving alloys of zinc/nickel and/or zinc/cobalt.

Obviously, the invention as conceived is susceptible of many modifications and variations, all of them falling within the scope of the appended claims.

Claims

1. A surface-treated metal wire for use in the realization of reinforcement structures for products made in elastomer material, of the type comprising a steel core provided with a metal alloy surface cladding, characterised in that the surface cladding is constituted by a zinc/manganese binary alloy with manganese content of between 5% and 80%.

2. A metal wire as in claim 1, characterised in that the manganese content in the cladding alloy is comprised between 30% and 70%.

3. A metal wire as in claim 1, characterised in that the surface cladding is formed by electrodeposition on a surface of the steel core.

4. A metal wire as in claim 1, characterised in that the layer of cladding exhibits a thickness comprised between 0.1 and 0.35 microns.

5. A metal wire as in claim 4, characterised in that it exhibits a diameter comprised between 0.15 and 0.35 mm.

6. A process for surface-cladding a metal wire for use in realizing reinforcement structures for products in elastomer material, said metal wire being of a type comprising a steel core provided with a surface cladding in metal alloy, characterised in that the process comprises at least one immersion phase of the steel core in an electrolytic bath containing zinc sulphate and manganese sulphate to cause a deposition of a layer of the surface cladding, said cladding being composed by a zinc/manganese binary alloy with manganese content comprised between 5% and 80%.

7. A process as in claim 6, characterised in that the electrolytic bath is constituted by a water solution containing:

   - zinc sulphate heptahydrate at between 10 and 90 gr/litre;
   - manganese sulphate monohydrate at between 20 and 100 gr/litre;
   - sodium citrate at between 115 and 230 gr/litre.

8. A process as in claim 7, characterised in that the electrolytic bath is maintained at a temperature chosen from a range of between 20 degrees celsius and 60 degrees celsius.

9. A process as in claim 7, characterised in that the electrolytic bath is maintained at a pH value comprised between 4 and 6.

10. A process as in claim 7, characterised in that a cathodic current density of between 5 and 40 A/dmq is applied to the electrolytic bath.

11. A process for surface-cladding a metal wire for realizing reinforcement structures for products made in elastomer material, of the type comprising a steel core provided with a metal alloy surface cladding,

characterised in that the process comprises phases of:

- immersion of the steel core in at least a first electrolytic bath containing manganese sulphate, to cause electrodeposition of manganese on the external surface of the core;
- immersion of the steel core in a second electrolytic bath containing zinc sulphate, to cause deposition of zinc on an external surface of the core;
- heat diffusion of the zinc and manganese to form the cladding layer of zinc/manganese alloy.

12. A process as in claim 11, characterised in that the first electrolytic bath comprises a water solution containing:

- manganese sulphate monohydrate at a level comprised between 80 and 120 gr/litre;
- ammonium sulphate comprised between 60 and 90 gr/litre; and
- ammonium thiocyanate comprised between 40 and 80 gr/litre.

13. A process as in claim 12, characterised in that the first electrolytic bath is maintained at a temperature comprised in a range from 20 degrees celsius and 40 degrees celsius.

14. A process as in claim 12, characterised in that the first electrolytic bath is maintained at a pH value comprised between 4.5 and 5.5.

15. A process as in claim 12, characterised in that a cathodic current density of between 15 and 25 A/dmq is applied to the first electrolytic bath.

16. A process as in claim 11, characterised in that the second electrolytic bath contains:

- zinc sulphate heptahydrate of between 300 and 450 gr/litre;
- sodium sulphate of between 50 and 70 gr/litre.

17. A process as in claim 16, characterised in that the second electrolytic bath is maintained at a temperature comprised between 20 degrees celsius and 30 degrees celsius.

18. A process as in claim 16, characterised in that the second electrolytic bath is maintained at a pH value of between 2 and 4.

19. A process as in claim 16, characterised in that a cathodic current density comprised between 20 and 40 A/dmq is applied to the second electrolytic bath.

20. A process as in claim 11, characterised in that the heat diffusion phase is effected by heating the metal wire by Joule effect.

21. A process for surface-cladding a metal wire for use in realizing reinforcement structures for products in elastomer material, said metal wire being of a type comprising a steel core provided with a surface cladding in metal alloy, characterised in that the process comprises phases of:

- immersion of the steel core in a first electrolytic bath containing zinc sulphate, to cause electrodeposition of zinc on the external surface of the core;
- immersion of the steel wire in at least a second electrolytic bath containing manganese sulphate, to cause deposition of manganese on the external surface of said steel wire;
- heat diffusion of the zinc and manganese to form a cladding layer in zinc/manganese alloy.

22. A process as in claim 21, characterised in that the first electrolytic bath contains:

- zinc sulphate heptahydrate at between 300 and 450 gr/litre;
- sodium sulphate at between 50 and 70 gr/litre.

23. A process as in claim 22, characterised in that the first electrolytic bath is maintained at a temperature chosen from a range of between 20 degrees celsius and 30 degrees celsius.

24. A process as in claim 22, characterised in that the first electrolytic bath is maintained at a pH value comprised between 2 and 4.

25. A process as in claim 22, characterised in that a cathodic current density comprised between 20 and 40 A/dmq is applied to the first electrolytic bath.

26. A process as in claim 21, characterised in that the second electrolytic bath comprises a water solution containing:

- manganese sulphate monohydrate at a level comprised between 80 and 120 gr/litre;
- ammonium sulphate comprised between 60 and 90 gr/litre; and
- ammonium thiocyanate comprised between 40 and 80 gr/litre.

27. A process as in claim 26, characterised in that the second electrolytic bath is maintained at a temperature chosen from a range comprised between 20 degrees celsius and 40 degrees celsius.

28. A process as in claim 26, characterised in that the second electrolytic bath is maintained at a pH value comprised between 4.5 and 5.5.

29. A process as in claim 26, characterised in that a cathode current density of between 15 and 25 A/dmq is applied to the second electrolytic bath.

30. A process as in claim 21, characterised in that the heat diffusion phase is effected by means of heating the metal wire by Joule effect.

31. A reinforcement structure of products made in elastomer material, comprising a plurality of cords each composed of a plurality of metal wires surface-treated as in claim 1.

32. A product made in elastomer material, incorporating a reinforcement structure as in claim 31.

33. A tyre for vehicle wheels, incorporating a reinforcement structure as in claim 31.

Patentansprüche

1. Oberflächenbehandelter Metalldraht für die Herstellung von Armierungsstrukturen für aus einem Elastomermaterial hergestellte Erzeugnisse, der einen Stahlkern umfaßt, der mit einer Oberflächenplattierung aus einer Metallegierung versehen ist, dadurch **gekennzeichnet,** daß die Oberflächenplattierung aus einer binären Zink-Mangan-Legierung mit einem Mangangehalt von 5 bis 80 % besteht.

2. Metalldraht nach Anspruch 1, dadurch **gekennzeichnet,** daß der Mangangehalt in der Plattierungslegierung 30 bis 70 % beträgt.

3. Metalldraht nach Anspruch 1, dadurch **gekennzeichnet,** daß die Oberflächenplattierung durch galvanische Abscheidung auf eine Oberfläche des Stahlkerns gebildet wird.

4. Metalldraht nach Anspruch 1, dadurch **gekennzeichnet,** daß die Plattierungsschicht eine Dicke von 0,1 bis 0,35 µm aufweist.

5. Metalldraht nach Anspruch 4, dadurch **gekennzeichnet,** daß er einen Durchmesser von 0,15 bis 0,35 mm aufweist.

6. Verfahren zur Oberflächenplattierung eines Metalldrahtes für die Herstellung von Armierungsstrukturen für aus einem Elastomermaterial hergestellte Erzeugnisse, der einen Stahlkern umfaßt, der mit einer Oberflächenplattierung aus einer Metalllegierung versehen ist, dadurch **gekennzeichnet,** daß das Verfahren wenigstens eine Stufe des Eintauchens des Stahlkerns in ein Elektrolysebad umfaßt, das Zinksulfat und Mangansulfat enthält, um die Abscheidung einer Schicht der Oberflächenplattierung zu bewirken, wobei die Plattierung aus einer binären Zink-Mangan-Legierung mit einem Mangangehalt von 5 bis 80 % besteht.

7. Verfahren nach Anspruch 6, dadurch **gekennzeichnet,** daß das Elektrolysebad aus einer wäßrigen Lösung besteht, die folgendes enthält:

10 bis 90 g/l Zinksulfatheptahydrat,
20 bis 100 g/l Mangansulfatmonohydrat und
115 bis 230 g/l Natriumcitrat.

8. Verfahren nach Anspruch 7, dadurch **gekennzeichnet,** daß das Elektrolysebad bei einer Temperatur, ausgewählt aus einem Bereich zwischen 20 und 60°C, gehalten wird.

9. Verfahren nach Anspruch 7, dadurch **gekennzeichnet,** daß das Elektrolysebad bei einem pH-Wert zwischen 4 und 6 gehalten wird.

10. Verfahren nach Anspruch 7, dadurch **gekennzeichnet,** daß an das Elektrolysebad eine Kathodenstromdichte von 5 bis 40 A/dm^2 angelegt wird.

11. Verfahren zur Oberflächenplattierung eines Metalldrahtes für die Herstellung von Armierungsstrukturen für aus einem Elastomermaterial hergestellte Erzeugnisse, der einen Stahlkern umfaßt, der mit einer Oberflächenplattierung aus einer Metalllegierung versehen ist, dadurch **gekennzeichnet,** daß das Verfahren folgende Stufen umfaßt:

Eintauchen des Stahlkems in wenigstens ein erstes Elektrolysebad, das Mangansulfat enthält, um die galvanische Abscheidung von Mangan auf der Außenfläche des Kerns zu bewirken,

Eintauchen des Stahlkerns in ein zweites Elektrolysebad, das Zinksulfat enthält, um die Abscheidung von Zink auf eine Außenfläche des Kerns zu bewirken und

Wärmediffusion des Zinks und Mangans zur Bildung der Plattierungsschicht aus der Zink-Mangan-Legierung.

12. Verfahren nach Anspruch 11, dadurch **gekennzeichnet,** daß das erste Elektrolysebad eine wäßrige Lösung umfaßt, die folgendes enthält:

80 bis 120 g/l Mangansulfatmonohydrat,

60 bis 90 g/l Ammoniumsulfat und
40 bis 80 g/l Ammoniumthiocyanat.

13. Verfahren nach Anspruch 12, dadurch **gekennzeichnet**, daß das erste Elektrolysebad bei einer Temperatur in einem Bereich zwischen 20 und 40°C gehalten wird.

14. Verfahren nach Anspruch 12, dadurch **gekennzeichnet**, daß das erste Elektrolysebad bei einem pH-Wert zwischen 4,5 und 5,5 gehalten wird.

15. Verfahren nach Anspruch 12, dadurch **gekennzeichnet**, daß an das erste Elektrolysebad eine Kathodenstromdichte von 15 bis 25 A/dm^2 angelegt wird.

16. Verfahren nach Anspruch 11, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad folgendes enthält:

300 bis 450 g/l Zinksulfatheptahydrat und
50 bis 70 g/l Natriumsulfat.

17. Verfahren nach Anspruch 16, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad bei einer Temperatur in einem Bereich zwischen 20 und 30°C gehalten wird.

18. Verfahren nach Anspruch 16, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad bei einem pH-Wert zwischen 2 und 4 gehalten wird.

19. Verfahren nach Anspruch 16, dadurch **gekennzeichnet**, daß an das zweite Elektrolysebad eine Kathodenstromdichte von 20 bis 40 A/dm^2 angelegt wird.

20. Verfahren nach Anspruch 11, dadurch **gekennzeichnet**, daß die Wärmediffusionsstufe durch Erwärmen des Metalldrahtes aufgrund des Joule-Effekts erfolgt.

21. Verfahren zur Oberflächenplattierung eines Metalldrahtes für die Herstellung von Armierungsstrukturen für aus einem Elastomermaterial hergestellte Erzeugnisse, der einen Stahlkern umfaßt, der mit einer Oberflächenplattierung aus einer Metallegierung versehen ist, dadurch **gekennzeichnet**, daß das Verfahren folgende Stufen umfaßt:

Eintauchen des Stahlkerns in ein erstes Elektrolysebad, das Zinksulfat enthält, um die galvanische Abscheidung von Zink auf der Außenfläche des Kerns zu bewirken,

Eintauchen des Stahldrahtes in wenigstens ein zweites Elektrolysebad, das Mangansulfat enthält, um die Abscheidung von Mangan auf der Außenfläche des Stahldrahtes zu bewirken und

Wärmediffusion von Zink und Mangan zur Bildung einer Plattierungsschicht aus der Zink-Mangan-Legierung.

22. Verfahren nach Anspruch 21, dadurch **gekennzeichnet**, daß das erste Elektrolysebad folgendes enthält:

300 bis 450 g/l Zinksulfatheptahydrat und
50 bis 70 g/l Natriumsulfat.

23. Verfahren nach Anspruch 22, dadurch **gekennzeichnet**, daß das erste Elektrolysebad bei einer Temperatur in einem Bereich zwischen 20 und 30°C gehalten wird.

24. Verfahren nach Anspruch 22, dadurch **gekennzeichnet**, daß das erste Elektrolysebad bei einem pH-Wert zwischen 2 und 4 gehalten wird.

25. Verfahren nach Anspruch 22, dadurch **gekennzeichnet**, daß an das Elektrolysebad eine Kathodenstromdichte von 20 bis 40 A/dm^2 angelegt wird.

26. Verfahren nach Anspruch 21, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad eine wäßrige Lösung umfaßt, die folgendes enthält:

80 bis 120 g/l Mangansulfatmonohydrat,
60 bis 90 g/l Ammoniumsulfat und
40 bis 80 g/l Ammoniumthiocyanat.

27. Verfahren nach Anspruch 26, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad bei einer Temperatur in einem Bereich zwischen 20 und 40°C gehalten wird.

28. Verfahren nach Anspruch 26, dadurch **gekennzeichnet**, daß das zweite Elektrolysebad bei einem pH-Wert von 4,5 bis 5,5 gehalten wird.

29. Verfahren nach Anspruch 26, dadurch **gekennzeichnet**, daß an das zweite Elektrolysebad eine Kathodenstromdichte von 15 bis 25 A/dm^2 angelegt wird.

30. Verfahren nach Anspruch 21, dadurch **gekennzeichnet**, daß die Wärmediffusionsstufe durch Erwärmen des Metalldrahtes aufgrund des Joule-Effekts erfolgt.

31. Armierungsstruktur von aus einem Elastomermaterial hergestellten Erzeugnissen, die eine Vielzahl von Kords umfaßt, von denen jeder aus einer Vielzahl von oberflächenbehandelten Metalldrähten

gemäß Anspruch 1 zusammengesetzt ist.

32. Erzeugnis, hergestellt aus einem Elastomermaterial, das eine Armierungsstruktur nach Anspruch 31 umfaßt.

33. Reifen für Kraftfahrzeugräder, die eine Armierungsstruktur nach Anspruch 31 umfassen.

Revendications

1. Fil métallique traité en surface, destiné à être utilisé pour la réalisation de structures de renforcement pour des produits en matière élastomère, du type comprenant un coeur en acier muni d'une enveloppe superficielle en alliage métallique, caractérisé en ce que l'enveloppe superficielle est constituée d'un alliage binaire zinc/manganèse ayant une teneur en manganèse comprise entre 5% et 80%.

2. Fil métallique selon la revendication 1, caractérisé en ce que la teneur en manganèse de l'alliage de l'enveloppe est comprise entre 30% et 70%.

3. Fil métallique selon la revendication 1, caractérisé en ce que l'enveloppe superficielle est formée par dépôt électrolytique sur une surface du coeur en acier.

4. Fil métallique selon la revendication 1, caractérisé en ce que la couche enveloppe présente une épaisseur comprise entre 0,1 et 0,35 micromètres.

5. Fil métallique selon la revendication 4, caractérisé en ce qu'il présente un diamètre compris entre 0,15 et 0,35 mm.

6. Procédé pour revêtir en surface un fil métallique destiné à être utilisé pour la réalisation de structures de renforcement pour des produits en matière élastomère, ledit fil. métallique étant du type comprenant un coeur en acier muni d'une enveloppe superficielle en alliage métallique, caractérisé en ce qu'il comprend au moins une phase d'immersion du coeur en acier dans un bain électrolytique contenant du sulfate de zinc et du sulfate de manganèse, pour provoquer le dépôt d'une couche de l'enveloppe superficielle, ladite enveloppe étant constituée d'un alliage binaire zinc/manganèse ayant une teneur en manganèse comprise entre 5% et 80%.

7. Procédé selon la revendication 6, caractérisé en ce que le bain électrolytique est constitué d'une solution aqueuse contenant :

- 10 à 90 g/l d'heptahydrate de sulfate de zinc,
- 20 à 100 g/l de monohydrate de sulfate de manganèse,
- 115 à 230 g/l de citrate de sodium.

8. Procédé selon la revendication 7, caractérisé en ce que le bain électrolytique est maintenu à une température comprise dans l'intervalle allant de 20 degrés celsius à 60 degrés celsius.

9. Procédé selon la revendication 7, caractérisé en ce que le bain électrolytique est maintenu à une valeur de pH comprise entre 4 et 6.

10. Procédé selon la revendication 7, caractérisé en ce que l'on utilise pour le bain électrolytique une densité de courant cathodique comprise entre 5 et 40 A/dm^2.

11. Procédé pour revêtir en surface un fil métallique destiné à la réalisation de structures de renforcement pour des produits en matière élastomère, du type comprenant un coeur en acier muni d'une enveloppe superficielle en alliage métallique, caractérisé en ce que le procédé comprend les étapes consistant à:

- immerger le coeur en acier dans au moins un premier bain électrolytique contenant du sulfate de manganèse, pour provoquer le dépôt électrolytique de manganèse sur la surface externe du coeur,
- immerger le coeur en acier dans un second bain électrolytique contenant du sulfate de zinc, pour provoquer le dépôt de zinc sur la surface externe du coeur,
- faire diffuser à chaud le zinc et le manganèse pour former la couche enveloppe en alliage zinc/manganèse.

12. Procédé selon la revendication 11, caractérisé en ce que le premier bain électrolytique est constitué d'une solution aqueuse contenant :

- 80 à 120 g/l de monohydrate de sulfate de manganèse,
- 60 à 90 g/l de sulfate d'ammonium, et
- 40 à 80 g/l de thiocyanate d'ammonium.

13. Procédé selon la revendication 12, caractérisé en ce que le premier bain électrolytique est maintenu à une température comprise dans l'intervalle allant de 20 degrés celsius à 40 degrés celsius.

14. Procédé selon la revendication 12, caractérisé en ce que le premier bain électrolytique est maintenu à une valeur de pH comprise entre 4,5 et 5,5.

15. Procédé selon la revendication 12, caractérisé en ce que l'on utilise pour le premier bain électrolytique

une densité de courant cathodique comprise entre 15 et 25 A/dm^2.

16. Procédé selon la revendication 11, caractérisé en ce que le second bain électrolytique contient :

- 300 à 450 g/l d'heptahydrate de sulfate de zinc,
- 50 à 70 g/l de sulfate de sodium.

17. Procédé selon la revendication 16, caractérisé en ce que le second bain électrolytique est maintenu à une température comprise dans l'intervalle allant de 20 degrés celsius à 30 degrés celsius.

18. Procédé selon la revendication 16, caractérisé en ce que le second bain électrolytique est maintenu à une valeur de pH comprise entre 2 et 4.

19. Procédé selon la revendication 16, caractérisé en ce que l'on utilise pour le second bain électrolytique une densité de courant cathodique comprise entre 20 et 40 A/dm^2.

20. Procédé selon la revendication 11, caractérisé en ce que l'on réalise l'étape de diffusion à chaud en chauffant le fil métallique par effet Joule.

21. Procédé pour revêtir en surface un fil métallique destiné à être utilisé pour la réalisation de structures de renforcement pour les produits en matière élastomère, ledit fil métallique étant du type comprenant un coeur en acier muni d'une enveloppe superficielle en alliage métallique, caractérisé en ce qu'il comprend les étapes consistant à:

- immerger le coeur en acier dans un premier bain électrolytique contenant du sulfate de zinc, pour provoquer le dépôt électrolytique de zinc sur la surface externe du coeur,
- immerger le fil en acier dans au moins un second bain électrolytique contenant du sulfate de manganèse, pour provoquer le dépôt de manganèse sur la surface externe dudit fil en acier,
- faire diffuser à chaud le zinc et le manganèse pour former une couche enveloppe en alliage zinc/manganèse.

22. Procédé selon la revendication 21, caractérisé en ce que le premier bain électrolytique contient :

- 300 à 450 g/l d'heptahydrate de sulfate de zinc,
- 50 à 70 g/l de sulfate de sodium.

23. Procédé selon la revendication 22, caractérisé en ce que le premier bain électrolytique est maintenu à une température comprise dans l'intervalle allant de 20 degrés celsius à 30 degrés celsius.

24. Procédé selon la revendication 22, caractérisé en ce que le premier bain électrolytique est maintenu à une valeur de pH comprise entre 2 et 4.

25. Procédé selon la revendication 22, caractérisé en ce que l'on utilise pour le premier bain électrolytique une densité de courant cathodique comprise entre 20 et 40 A/dm^2.

26. Procédé selon la revendication 21, caractérisé en ce que le second bain électrolytique est constitué d'une solution aqueuse contenant :

- 80 à 120 g/l de monohydrate de sulfate de manganèse,
- 60 à 90 g/l de sulfate d'ammonium, et
- 40 à 80 g/l de thiocyanate d'ammonium.

27. Procédé selon la revendication 26, caractérisé en ce que le second bain électrolytique est maintenu à une température comprise dans l'intervalle allant de 20 degrés celsius à 40 degrés celsius.

28. Procédé selon la revendication 26, caractérisé en ce que le second bain électrolytique est maintenu à une valeur de pH comprise entre 4,5 et 5,5.

29. Procédé selon la revendication 26, caractérisé en ce que l'on utilise pour le second bain électrolytique une densité de courant cathodique comprise entre 15 et 25 A/dm^2.

30. Procédé selon la revendication 21, caractérisé en ce que l'on réalise l'étape de diffusion à chaud en chauffant le fil métallique par effet Joule.

31. Structure de renforcement de produits en matière élastomère, qui comprend plusieurs câblés dont chacun est constitué de plusieurs fils métalliques traités en surface selon la revendication 1.

32. Produit en matière élastomère, dans lequel est incorporée une structure de renforcement selon la revendication 31.

33. Pneu pour roue de véhicule, dans lequel est incorporée une structure de renforcement selon la revendication 31.

FIG. 1

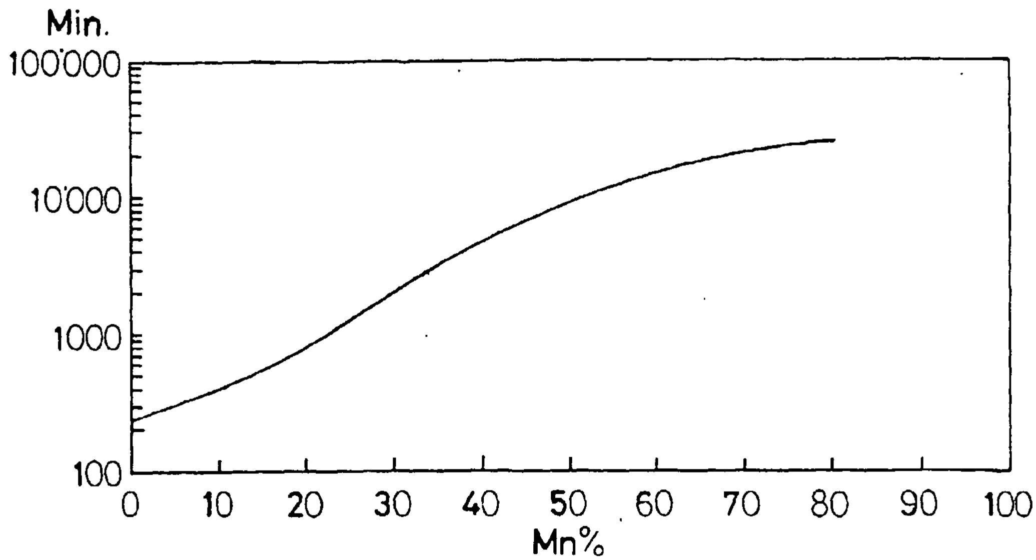

FIG. 2

Rivestimento	Tempo di formazione Ruggine (min.)
Ottone	30
Zn	240
ZnCo	1152
NiZn/ZnCo	1720
ZnMn 5%	360
ZnMn 30%	2400
ZnMn 60%	20000

FIG. 3

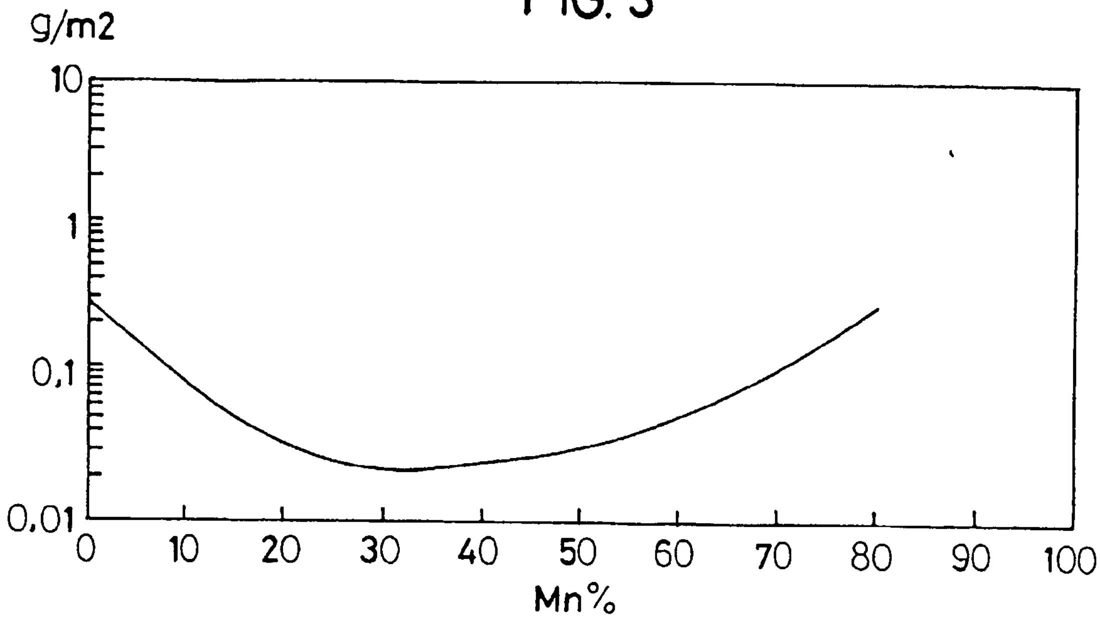

FIG. 4

Rivestimento	F (N)
Ottone 70/30	2350
Zn 100%	2005
Zn/Mn (5-80%)	2310
Mn 100%	1427